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Thermodynamic Forecasts of the Mediterranean Sea Acidification

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Abstract

Anthropogenic CO_2 is a major driver of the present ocean acidification. This latter is threatening the marine ecosystems and has been identified as a major environmental and economic menace. This study aims to forecast from the thermodynamic equations, the acidification variation (ΔpH) of the Mediterranean waters over the next few decades and beyond this century. In order to do so, we calculated and fitted the theoretical values based upon the initial conditions from data of the 2013 MedSeA cruise. These estimates have been performed both for the Western and for the Eastern basins based upon their respective physical (temperature and salinity) and chemical (total alkalinity and total inorganic carbon) properties. The results allow us to point out four tipping points, including one when the Mediterranean Sea waters would become acid (pH<7).

In order to provide an associated time scale to the theoretical results, we used two of the IPCC (2007) atmospheric CO_2 scenarios. Under the most optimistic scenario of the "Special Report: Emissions Scenarios" (SRES) of the IPCC (2007), the results indicate that in 2100, pH may decrease down to 0.245 in the Western basin and down to 0.242 in the Eastern basin (compared to the pre-industrial pH). Whereas for the most pessimistic SRES scenario of the IPCC (2007), the results for the year 2100, forecast a pH decrease down to 0.462 and 0.457, for the Western and for the Eastern basins, respectively. Acidification, which increased unprecedentedly in recent years, will rise almost similarly in both Mediterranean basins only well after the end of this century. These results further confirm that both basins may become undersaturated (< 1) with respect to calcite and aragonite (at the base of the mixed layer depth), only in the far future (in a few centuries).

Keywords: Anthropogenic CO_2, Seawater acidification, Modeling, Carbonate system, critical points, Mediterranean Sea.

Introduction

Oceanic uptake of anthropogenic carbon dioxide (C_{ANT}) is altering the seawater chemistry of the world's oceans with various consequences on marine ecosystems. Ocean acidification is one of the consequences of approximately 79 million tons of carbon dioxide (CO_2) released into the atmosphere every day from fossil fuel burning, deforestation and cement production (IPCC, 2007; IPCC,2013). As a result of human activities, today's atmospheric CO_2 concentration is rising at a rate of ~ 0.5% year^{-1} (Forster *et al.*, 2007), which is ~100 times faster than any change during the past 650 000 years (Royal Society, 2005; Siegenthaler *et al.*, 2005). The atmospheric increase of CO_2 from 2012 to 2013 was 2.9 microatmosphere (matm), which is the largest annual increase for the period 1984-2013 (WMO, 2014). Oceans play a key role in the mitigation of the increasing atmospheric pCO_2. Approximately 25% of the total human emissions of CO_2 to the atmosphere is accumulating into the ocean (Sabine *et al.*, 2004; Mikaloff-Fletcher *et al.*, 2006; Le Quéré *et al.*, 2010; Sabine *et al.*, 2011; Le Quéré *et al.*, 2015). Without this buffer capacity of the oceans, the CO_2 content in the atmosphere would have been much higher and global warming and its consequences more dramatic.

Today there is a rapid population growth on the Mediterranean coast, from 165 million inhabitants in 2000 to 187 million in 2007, an increase of 13% (Eurostat, 2009). Although the Mediterranean Sea represents less than 1% of the global world's ocean surface (UNEP/MAP-Plan Bleu, 2009), it is under important anthropogenic pressure. Thus, the Mediterranean Sea is acidifying quickly and its marine ecosystems are under stress. A surface pH decrease of 0.05 unit has been recorded since the pre-industrial era (Dore *et al.*, 2009; Bates *et al.*, 2012) and models predict an additional pH decline by 0.3-0.5 pH unit during the 21st century depending upon which Intergovernmental Panel on Climate Change (IPCC) CO_2 emission scenario (Caldeira & Wickett, 2005 ; Orr *et al.*, 2005a; Feely *et al.*, 2009) is used for the forecast. In the Mediterranean Sea, Géri *et al.* (2014) forecasted an evolution ranging between 0.3 and 0.4 pH unit decrease in the surface water of the Northwestern Mediterranean Sea by the end of this century. A few other studies (Àlvarez *et al.*, 2014; Schneider *et al.*, 2010; Touratier &

Goyet, 2011; Orr, 2011; Palmiéri *et al.*, 2015) estimated the present and future situation of the seawater acidification in the Mediterranean waters, particularly in the deep waters, and its influences on marine organisms, community structure and the entire ecosystems. They suggest that the acidification variations in the Mediterranean Sea are close but slightly higher than the ones estimated in the global ocean.

In this paper, based mainly upon the chemical thermodynamic equilibrium equations of the CO_2/carbonate system in seawater (DOE, 1994), we first calculated the acidification variations (ΔpH) due to the C_{ANT} penetration both into the Western and into the Eastern Mediterranean basins. The objectives are first to show the importance and impact of the thermodynamic equilibrium of the CO_2/carbonate system on ocean acidification, and second to highlight the significant geographical variations. Then, in order to present not only discrete but also continuous estimates of acidification, we fitted these results with simple functions (one for each basin). Subsequently, we present and discuss, the impacts of this acidification on the carbonate saturation states in the Mediterranean Sea, as well as four tipping points (corresponding to points of significant changes in the biogeochemical seawater property), related to the Mediterranean Sea acidification.

Methodology

Data set

In order to illustrate the largest difference that can occur in the Mediterranean Sea we choose as initial conditions, data from two stations located at the extreme Northwestern and Eastern sides of the Mediterranean Sea. These two punctual locations were chosen to be relatively far from each other (rather taking an average of the data over each basin), to highlight the large range of variations in the Mediterranean Sea.

Hydrologic properties [salinity, S and temperature, T (ºC)] were measured *in situ* and described earlier (Hassoun *et al*., 2015a). The precisions of the measurements were ± 0.001 ºC for T, and ± 0.0003 for S. For total alkalinity (A_T) and total dissolved inorganic carbon (C_T), seawater samples were collected at all stations of the MedSeA cruise (May 2 – June 2, 2013), throughout the water column. These samples were then carefully measured onshore by a potentiometric titration in a closed cell (Hassoun *et al*., 2015a,b,c). The accuracy of A_T and C_T measurements was determined to be ± 2 µmol.kg^{-1} for A_T and ± 4 µmol.kg^{-1} for C_T (Hassoun *et al.,* 2015b,c; Gemayel *et al*., 2015).

Next, in section 2.2, we describe the calculation of the theoretical pH variations, at the base of the wintertime mixed layer depth, as a function of theoretical anthropogenic carbon concentrations ranging from 0 to 700 µmol.kg^{-1} (corresponding to about 10 times the present anthropogenic carbon concentrations).

Thermodynamic equations

We used the well known thermodynamic equilibrium equations:

$$[CO_2^*] + [H_2O] \Leftrightarrow [H^+] + [HCO_3^-] \quad (I)$$
$$[HCO_3^-] \Leftrightarrow [H^+] + [CO_3^{2-}] \quad (II)$$

as described in details in the Handbook of Methods for Analysis of the Various Parameters of the Carbon Dioxide System in Seawater (DOE, 1994), with the apparent constants:

$$K_1 = [H^+]\,[HCO_3^-] / [CO_2^*] \quad (III)$$
$$\text{and } K_2 = [H^+]\,[CO_3^{2-}] / [HCO_3^-] \quad (IV)$$

where brackets represent total stoichiometric concentrations of the particular chemical species enclosed. $[CO_2^*]$ represents the sum of the concentrations of the aqueous CO_2 and H_2CO_3 species. Thus, using these equations, it is possible to calculate (via CO2SYS or other similar software), the variations of pH from a constant A_T and C_T variations, at any given sea-surface temperature (SST) and sea-surface salinity (SSS).

Forecast of pH variations as a function of anthropogenic carbon

In order to forecast the Mediterranean Sea acidification beyond the end of the next century, we calculate pH from the measured A_T (A_T^m) at the base of the wintertime mixed layer depth (Table 1) and a theoretical C_T calculated as follows:

Table 1. The 2013 measured S, T, A_T, C_T at the base of the wintertime mixed layer depth and the calculated $C_{Tpreindustrial}$ and $pH_{preindustrial}$ in the Western and Eastern basins of the Mediterranean Sea.

Parameters	Latitude (°N)	Longitude (°E)	Mixed Layer Depth (m)	S^m	T^m (ºC)	A_T^m (µmol. kg^{-1})	C_T^m (µmol. kg^{-1})	pH^c	pH^{preind}	C_T^{preind} (µmol. kg^{-1})
Western basin	40.0736	5.94744	150	37.9812	13.487	2537	2261	8.087	8.215	2181
Eastern basin	34.22416	33.22504	200	39.0775	15.845	2634	2311	8.099	8.225	2224

At a given year, C_T was calculated by adding a theoretical C_{ANT} concentration to the preindustrial C_T concentration (C_T^{preind}) , as follows:

$$C_T = C_T^{preind} + C_{ANT} \quad \text{(I)}$$

In order to calculate C_T^{preind} we made the assumption that the temporal variation of CO_2 fugacity (fCO_2) in seawater follows that of the atmosphere. Thus, C_T^{preind} is calculated from A_T^m, S^m, T^m, (fCO_2^c – 116), where fCO_2^c is calculated from A_T^m, S^m, T^m, C_T^m. The number "116" is the difference between the atmospheric preindustrial fCO_2 = 280 matm and the measured atmospheric 2013 fCO_2 = 396 matm (NOAA; http://co2now.org/current-co2/co2-now), thus 396 – 280 =116 matm.

In order to provide a forecast over a very long range, we choose the theoretical values of C_{ANT} to increase from 0 to 700 mmol.kg^{-1} (corresponding to about ten times the actual penetration of anthropogenic carbon in the Mediterranean Sea), by steps of 1 mmol.kg^{-1}.

pH^c was then calculated from T^m, A_T^m (Table 1), and C_T^m (Table 1 and Eq.I). The calculation was made according to the output conditions of temperature and pressure, based on the A_T-C_T combination and choosing the set of apparent constants (K_1 and K_2) of Goyet & Poisson (1989), the sulfate constants of Dickson (1990), the seawater scale and the borate constants of Uppström (1974). Note that the choice of constants here is not very important since we are looking at variations. The pre-industrial pH (pH^{preind}; Table 1) was calculated from the measured A_T^m (since A_T is not affected by the accumulation of C_{ANT} in seawater) and C_T^{preind} (from {A_T^m, S^m, T^m, [fCO_2^c – 116]} as mentioned above).

Thereafter, the pH variation (ΔpH) is calculated from the computed pH and the pre-industrial pH as follows:

$$\Delta pH = pH - pH_{preind} \quad \text{(II)}$$

For each basin, we then fitted the discrete values of ΔpH as a function of C_{ANT}.

Results and Discussion

Acidification estimates of the Mediterranean Sea

Figure 1 shows, that the largest difference in DpH between the Western and the Eastern basins of the Mediterranean Sea will occur when C_{ANT} will range from 100 µmol.kg^{-1} to 700 µmol.kg^{-1}. This is due to the different oceanographic characteristics (T, S, A_T, and C_T) in each main basin. However, beyond this C_{ANT} range (not shown here), the chemical equilibrium of the CO_2/carbonate system in seawater will induce very similar variations of pH (ΔpH).

Note that the difference between the two chosen locations (one in the Western basin, the other in the Eastern basin) is significant (up to 0.12 pH unit). Thus this indicates that ocean acidification is highly dependent upon the chemical properties of seawater and thus, will strongly vary from one location to another.

Figure 1, clearly illustrates the seawater buffer effect, and thus the non-linear variation of pH as a function of C_{ANT} penetration. From C_{ANT} = 0 to C_{ANT} = 700 µmol.kg^{-1}, ΔpH will vary by less than -1.5 pH unit. Consequently, Fig.1 shows that the largest Mediterranean Sea pH decrease due to massive input of anthropogenic carbon (C_{ANT} > 600 µmol.kg^{-1}) would remain close to -1.5 pH unit. Thus, the results of this model provide a reasonable limit of pH variations for future laboratory and mesocosms studies.

In addition, Table 1 indicates that at ΔpH = -1.215 for the Western Mediterranean Sea (or at ΔpH = -1.225 for the Eastern Mediterranean Sea), the seawater pH will be neutral (pH = 7.00). Thus, the corresponding (.1) addition of C_{ANT} (548 µmol.kg^{-1} and 591 µmol.kg^{-1}, for the Western and Eastern basins the Mediterranean Sea, respectively), indicates points beyond which, the Mediterranean Sea waters will become acid (pH < 7.00). These points, called "Tipping Point" pH7 (TP_{pH7}), are shown in Figure 2.

In the Western basin, ΔpH follows a simple polynomial function of degree 7 (Eq.III) of C_{ANT}:

$$\Delta pH = 0.03895\ X^7 - 0.03946\ X^6 - 0.1747\ X^5 + 0.2054\ X^4 + 0.07289\ X^3 + 0.0001649\ X^2 - 0.3497\ X - 1.915 \quad \text{(III)}$$

with X = (C_{ANT} – 1500)/866.5 where the number "1500" represents the mean of C_{ANT} (since for an improved accuracy of the equation, we choose 0 < C_{ANT} < 3000 µmol.kg^{-1}), and the number "866.5" represents the C_{ANT} standard deviation. The r^2 = 0.9996 of equation III indicates the goodness of this fit.

In the Eastern basin, ΔpH also follows a simple polynomial function of degree 7 (Eq.IV) of C_{ANT}:

$$\Delta pH = 0.0363\ X^7 - 0.0476\ X^6 - 0.1453\ X^5 + 0.2213\ X^4 + 0.009255\ X^3 + 0.01867\ X^2 - 0.3486\ X - 1.918 \quad \text{(IV)}$$

with X still equals to (C_{ANT} – 1500)/866.5. The r^2 = 0.9997 of equation IV indicates the goodness of this fit.

These fits (Eq.III and Eq.IV) are provided to forecast the pH variations in each basin of the Mediterranean Sea, based only upon C_{ANT} concentrations with 0 < C_{ANT} < 3000 µmol.kg^{-1}. Thus, inversely, it could be possible to estimate C_{ANT} from accurate measurements of DpH over several years (decades).

In Figure 2, compared with Figure1, we have added two strait lines, which are the linear fits of each curve in the range 0 < C_{ANT} < 70 µmol.kg^{-1} (corresponding to the present C_{ANT} penetration in the Mediterranean Sea; Hassoun *et al.*, 2015c), as well as the four tipping points (TP_{pH7} is described above, the others are described below), for the Western and Eastern basins of the Mediterranean Sea. Figure 2 demonstrates that from now on, a linear interpolation will provide an unrealistic, very optimistic forecast of (small) pH decrease.

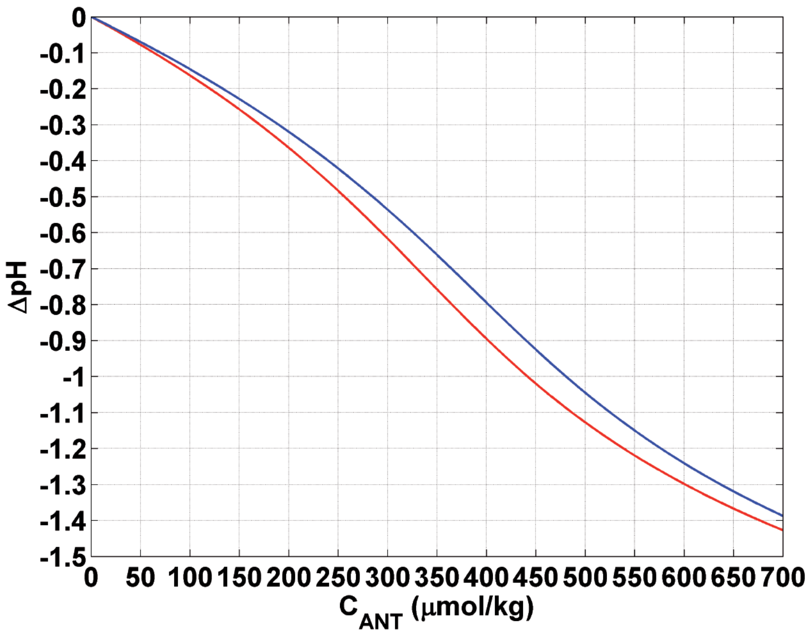

Fig. 1: Theoretical estimates of pH variations as a function of C_{ANT} ($0 < C_{ANT} < 700$ µmol.kg^{-1}) in the Western (red curve) and Eastern basins (blue curve) of the Mediterranean Sea.

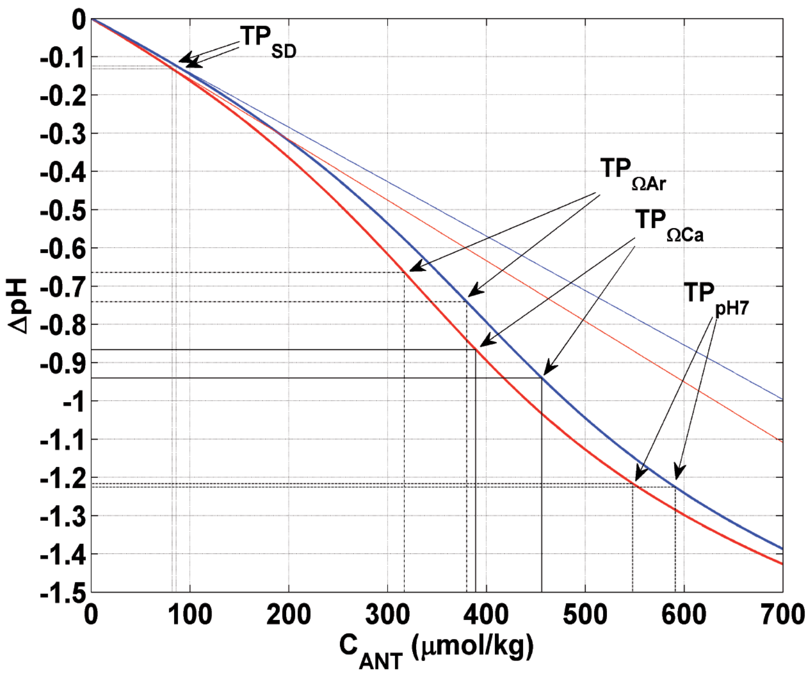

Fig. 2: Theoretical estimates of pH variations as a function of C_{ANT} in the Western and Eastern basins of the Mediterranean Sea. The red and blue strait lines are the linear fits of the red and blue curves in the range $0 < C_{ANT} < 70$ µmol.kg^{-1}, respectively (Equations: $\Delta pH = -\ 0.00158439\ C_{ANT}$ [red] and $\Delta pH = -\ 0.00142387\ C_{ANT}$ [blue]).

The chemical properties of seawater have now reached a point where a small addition of anthropogenic carbon will induce a non-linear, relatively large pH drop (Fig. 2). This is happening now. As anthropogenic carbon continually penetrates into the Mediterranean Sea, the pH decreases more sharply from one day to the next.

The differences between DpH of the linear fits and the theoretical DpH (curves) as a function of C_{ANT} (< 700 µmol.kg^{-1}), are shown in Figure 3. This figure illustrates clearly a tipping point of "Sharp Decrease" in pH (TP_{SD}), at C_{ANT} = 82 µmol.kg^{-1} for the Western Mediterranean Sea (and at C_{ANT} = 86 µmol.kg^{-1} for the Eastern Mediterranean Sea), where the variation of pH deviates from a linear relationship with C_{ANT} penetration, and where a small addition of C_{ANT} induces a sharp decrease in pH. Thus, today, a small additional input of

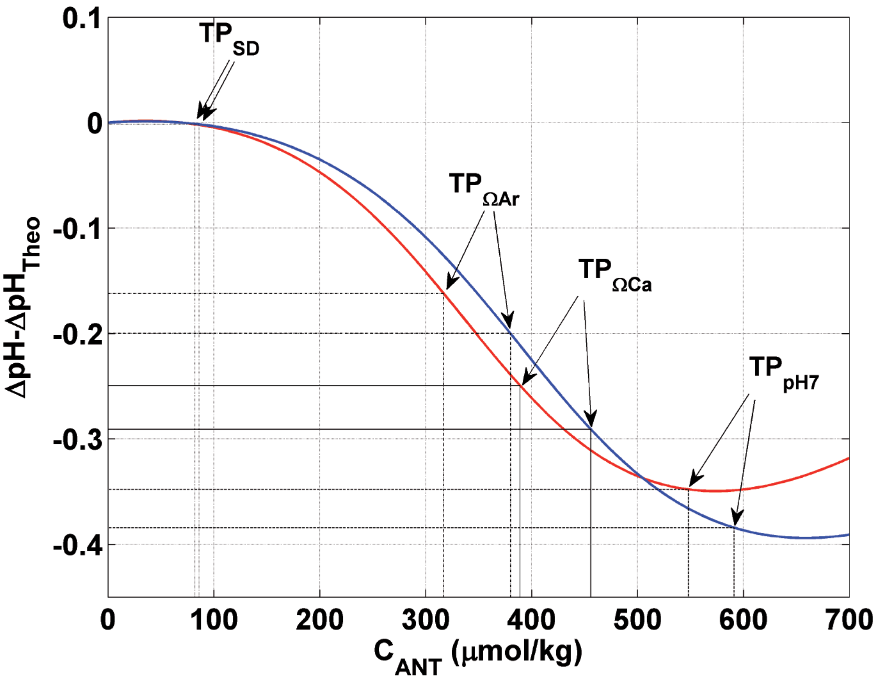

Fig. 3: The distribution of differences between the experimental and theoretical ΔpH as a function of anthropogenic CO_2.

anthropogenic carbon into the Mediterranean Sea would have a more significant impact than in the past, on its acidification and therefore on its ecosystems.

What are the consequences of the increasing anthropogenic CO_2 concentrations on the calcium carbonate (calcite and aragonite) saturation states in the Mediterranean Sea waters?

In order to assess the influence of the increasing C_{ANT} concentrations, we also computed (via the program "CO2Sys"), the calcium carbonate saturation via the two forms calcite and aragonite (Ω_{Ca} and Ω_{Ar}). As a reminder, Ω_{Ca} and Ω_{Ar} are proportional to the product of concentrations of calcium ions and carbonate ions dissolved in seawater (Ω_i = Cste x [Ca^{++}] x [CO_3^{--}]).

When $\Omega_i > 1$, there is oversaturation of the dissolved calcium carbonate. Thus, it will tend to precipitate. Corals and coralline sand are mainly made of calcite. Aragonite, which is mainly the result of the slow transformation of calcite, is mainly found in fossils.

When Ω_{Ar} (or Ω_{Ca}) is < 1, there is under-saturation of the dissolved calcium carbonate. Thus, it will tend to dissolve (shell and skeleton formation cannot occur). In seawater Ω_{Ar} is always inferior to Ω_{Ca}; aragonite is more soluble than calcite.

Therefore, the determination of when $\Omega_{Ar} = 1$ and $\Omega_{Ca} = 1$ will provide two tipping points ($TP_{\Omega Ar}$ and $TP_{\Omega Ca}$), for the ecosystem equilibrium. The results indicate that these tipping points when $\Omega_{Ar} = 1$ and $\Omega_{Ca} = 1$, will occur when C_{ANT} = 317 µmol.kg^{-1} and C_{ANT} = 389 µmol.kg^{-1}, respectively for the Western Mediterranean Sea, and when C_{ANT} = 380 µmol.kg^{-1} and C_{ANT} = 456 µmol.kg^{-1}, respectively for the Eastern Mediterranean Sea. They are shown on Figures 2 and 3.

When would these four tipping points (TP_{SD}, $TP_{\Omega Ar}$, $TP_{\Omega Ca}$, and TP_{pH7}), occur in the Mediterranean Sea waters?

Taking into account that fCO_2 in seawater (fCO_2^{sw}), follows that (fCO_2^{air}) of the atmosphere (Royal Society, 2005; Bates *et al.*, 2012; Zeebe, 2012), we can calculate the estimated anthropogenic carbon concentrations over the years as follows:

1) First, we can use results from both the most optimist/ecological (B1; fCO_2^{air} = 485 matm and 540 matm for year 2050 and 2100, respectively) and the most pessimistic (A1F1; fCO_2^{air} = 570 matm and 940 matm for year 2050 and 2100, respectively) of the SRES scenarios (IPCC 2007) to make such estimates at least to year 2100.

2) Then, assuming that ΔfCO_2 (fCO_2^{sw} - fCO_2^{air}) remains constant over time, we can compute the concentrations of anthropogenic carbon that penetrates into the seawater. This was done by determining the difference between the initial C_T and C_T calculated using the constant total alkalinity, salinity, temperature, and an increasing fCO_2^{sw} (parallel to the fCO_2^{air} curve). Thus, for the Western basin, based upon the first scenario (B1), the C_{ANT} concentrations would be in the order of 122 and of 144 µmol kg^{-1} for the years 2050 and 2100, respectively, and based upon the second scenario (A1F1), C_{ANT} concentrations would be close to 154 and 241 µmol.kg^{-1} for the years 2050 to 2100, respectively (Fig. 4). For the Eastern basin, based upon

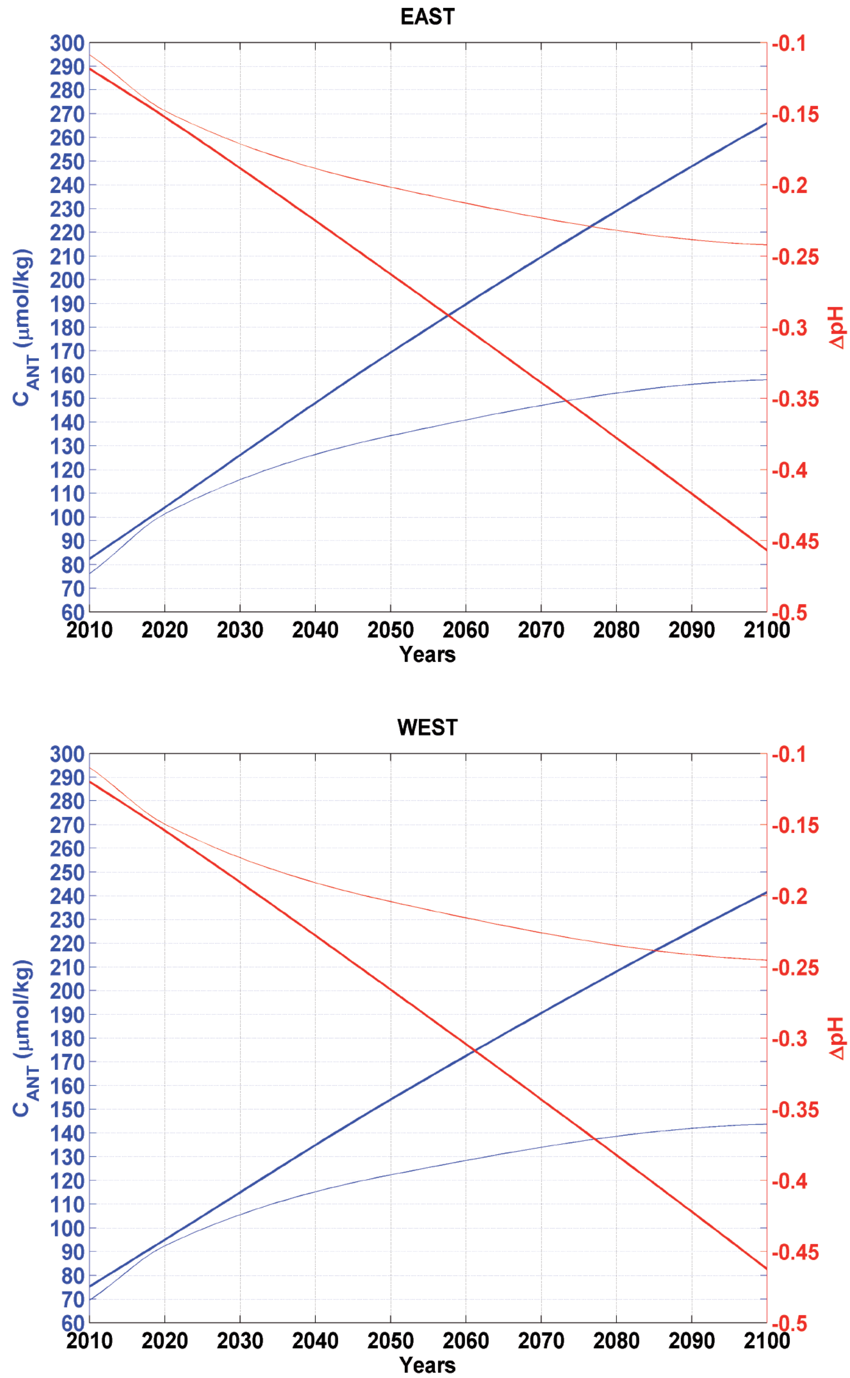

Fig. 4: Variations of the anthropogenic CO_2 (left y axis in blue) and acidification (ΔpH; right y axis in red) in the a) Western Mediterranean basin and b) Eastern Mediterranean basin, from 2013 to the end of the 21st century (2100) according to the B1 (thin lines) and A1F1 (thick lines) SRES scenarios of the IPCC (2007).

scenario B1, the C_{ANT} concentrations would be in the order of 134 and of 158 µmol kg^{-1} for the years 2050 and 2100, respectively, and based upon scenario A1F1, C_{ANT} concentrations would be close to 169 and 266 µmol.kg^{-1} for the years 2050 to 2100, respectively (Fig. 4).

The results indicate that when C_{ANT} is equal to 240 µmol.kg^{-1} in seawater (about year 2100 according to scenario A1F1), the acidification variation will reach a value of 0.459 and 0,401pH unit in the Western and Eastern basins, respectively.

The variations of pH and anthropogenic CO_2 concentrations until the end of the 21st century are displayed in Figure 4. Estimated acidification variations from the present until the end of this century are presented in Table 2 for the two extreme SRES scenarios of the IPCC (2007). The results confirm that up to the end of this century, the Western basin (Fig. 4a) is always more acidified than the Eastern one (Fig. 4b). Figure 4a,b further illustrates the differences of acidification according to the two scenarios. Thus, by the end of this century, the

Table 2. The present and future Mediterranean Sea pH according to the anthropogenic CO_2 based on two extreme SRES scenarios of the IPCC (2007). B1 is the most optimistic scenario while A1F1 is the most pessimistic one.

Year	ΔfCO_2^{air} (µatm)		C_{ANT} (µmol.kg^{-1}) West/East		pH (pH unit) Western basin		Eastern basin	
	B1	*A1F1*	*B1*	*A1F1*	*B1*	*A1F1*	*B1*	*A1F1*
2020	140	145	92/101	95/104	8.065	8.061	8.077	8.073
2050	205	290	122/134	154/169	8.011	7.949	8.024	7.962
2100	260	660	144/158	241/266	7.970	7.753	7.983	7.768

expected decrease in pH in the Western basin will range from 0.245 to 0.462 (from 0.242 to 0.457 in the Eastern basin).

Note that for these calculations we assumed that the seawater temperature did not change. If we take into account the probable increase in seawater temperature, the penetration of atmospheric CO_2 into the seawater will decrease, and thus slow down the penetration of anthropogenic carbon in seawater. For instance, a temperature increase of 2°C by 2050 (IPCC SRES scenarios; 2007) will reduce C_{ANT} by approximately 15 µmol.kg^{-1} and an increase of 4.5°C by 2100 (IPCC SRES scenarios; 2007), will reduce C_{ANT} by approximately 30 µmol.kg^{-1}. Thus, such temperature increase would induce in 2100 a pH variation ranging only from -0.19 to -0.37 pH unit. The amplitude of such pH decrease would, consequently, remain within the observed amplitude of the seasonal variations (Middelboe & Hansen, 2007; Abdelmongy & El-Moselhy, 2015). Similar results were observed in recent global modeling studies (Orr *et al*., 2005; Somot *et al*., 2008; Orr, 2011; Palmiéri *et al*., 2015), which took into account the variations in ocean circulation, seawater temperature, and air-sea CO_2 fluxes.

At the global ocean scale, modelers have noted a decrease of 0.1 pH unit, between 1750 and 1994, in the ocean surface layers (equivalent to a 30% increase of $[H^+]$ ions ; Sabine *et al.*, 2004 ; Raven *et al.*, 2005 ; Orr *et al.*, 2005). However, time-series studies conducted in the North Pacific Ocean between 1988 and 2007 (Dore *et al.*, 2009) and in the North Atlantic Subtropical gyre between 1983 and 2011 (Bates *et al.*, 2012) have documented a significant long-term decreasing trend of 0.05 pH unit (0.0019 and 0.0017 unit yr^{-1} in the North Pacific and the North Atlantic respectively). At the end of the century, the model from Caldeira & Wickett (2003) predicted an increased acidification with a pH decrease between 0.3 and 0.4 pH unit. Similarly, Géri *et al.* (2014) and Yao *et al.* (2016) predicted the same range of pH decrease (0.3-0.4 pH unit) in the northwestern part of the Mediterranean Sea.

Table 3 shows the results of calcium carbonate ions (calcite and aragonite) saturations at the base of the mixed layer depth, for both the Western and Eastern basins.

While the main changes are largest at the ocean surface, the penetration of anthropogenic CO_2 into the ocean interior will alter the chemical composition over the 21st century down to several thousand meters (IPCC, 2014). Thus, as expected Ω_{Ca} and Ω_{Ar} decrease with the increasing C_{ANT} and acidification level (Table 3). According to the most pessimistic (A1F1) scenario of the IPCC (2007), the results show that the Mediterranean Sea waters will remain oversaturated with respect to calcite and aragonite until the end of this century (Table 3). Consequently, the impacts of the Mediterranean Sea acidification on calcareous shells would probably be very light until the end of this century. Yet, afterwards both basins will become undersaturated with respect to aragonite as soon as C_{ANT} = 380 µmol.kg^{-1} would have penetrated into the Mediterranean Sea. Both basins will then become undersaturated with respect to calcite as soon as C_{ANT} = 456

Table 3. The present and future Mediterranean calcium carbonate saturations (calcite, Ω_{Ca} and aragonite, Ω_{Ar}) at the base of the mixed layer depth, according to the anthropogenic CO_2 based on two extreme SRES scenarios of the IPCC (2007). B1 is the most optimistic scenario while A1F1 is the most pessimistic one.

Year	C_{ANT} (µmol.kg^{-1}) West/East		Western basin				Eastern basin			
			B1		*A1F1*		*B1*		*A1F1*	
	B1	*A1F1*	**ΩCa**	**ΩAr**	**ΩCa**	**ΩAr**	**ΩCa**	**ΩAr**	**ΩCa**	**ΩAr**
2020	92/101	95/104	4.37	2.81	4.33	2.79	5.04	3.26	5.00	3.23
2050	122/134	154/169	3.94	2.54	3.50	2.25	4.56	2.95	4.06	2.63
2100	144/158	241/266	3.64	2.34	2.35	1.51	4.23	2.74	2.77	1.79

μmol.kg^{-1} would have penetrated in the Mediterranean Sea. Therefore, long before the Mediterranean Sea will become acid (pH < 7; C_{ANT} > 591 μmol.kg^{-1}), marine organisms depending upon formation of calcareous shells and skeletons will be highly vulnerable.

When water is undersaturated with respect to calcium carbonate ions, marine organisms can no longer form calcium carbonate shells (Raven *et al.*, 2005). Increasing atmospheric CO_2 concentrations lower oceanic pH and carbonate ion concentrations, thereby decreasing the saturation state with respect to calcium carbonate minerals (Feely *et al.*, 2004). The main driver of these changes is the direct geochemical effect due to the addition of anthropogenic CO_2 to the surface ocean (IPCC, 2007). After investigating the effects of CO_2-induced ocean acidification on calcification in 18 benthic marine organisms, Ries *et al.* (2009) suggested that the response of calcifying marine organisms to elevated atmospheric fCO_2 will be variable and complex. They found that oysters, scallops, and temperate corals grew thinner, weaker shells as acidity levels were increased. However, they indicated that some species, including blue crabs, lobsters, and shrimp, grew thicker shells that could make them more resistant to predators. Nevertheless, Mediterranean surface waters would remain oversaturated with respect to calcite and aragonite in surface layers (CIESM, 2008). However, the increasing acidification level could considerably decrease this saturated state by the end of this century. Although it may be assumed that the dissolution of calcium carbonate ions is not thermodynamically favorable and therefore not an anticipated problem in the Mediterranean Sea (CIESM, 2008), results from Table 3 suggest that over the very long term (beyond the next century), this may become an issue.

High acidification levels can also influence the speciation of nutrients [the degree of limitation of phosphate ions, already a limiting factor for primary production (Berland *et al.*, 1980), will increase], and their trophic situations (worsening oligotrophy). This potentially affects the productivity, the entire structure of food webs as well as the carbon export.

Summary

In this paper, based upon the thermodynamic equations of the chemical equilibrium of the CO_2/carbonate system in seawater we first calculated the variation of pH (ΔpH) as a function of theoretical C_{ANT} concentrations ranging from 0 μmol.kg^{-1} to 700 μmol.kg^{-1}, at the base of the mixed layer depth in waters of the Western and Eastern basins of the Mediterranean Sea. We then fitted these results with simple polynomial functions (one for each basin; Eq.III and IV for the Western and Eastern basin, respectively). The results show that the Western basin is acidifying faster than the Eastern basin. The difference in acidification between these two basins would reach its maximum (ΔpH = 0.101) when C_{ANT} would reach 395 μmol.kg^{-1}.

The results show that a linear approximation cannot be used for C_{ANT} larger than 86 μmol.kg^{-1} since it will largely underestimates the pH variations. Thus, these results indicate the first tipping point (TP_{SD}) when the Mediterranean Sea acidification will sharply increase compared to the regular increase of C_{ANT}. This is happening now!

In order to provide an estimate of the dates corresponding to these variations, we made the reasonable assumption that surface seawater fCO_2 follows that of the atmosphere. Thus, based upon the SRES scenario B1 (optimist) and A1F1 (pessimistic) of the IPCC (2007), we could estimate the pH variations as a function of time. Therefore, by the end of this century, when C_{ANT} could reach 144 μmol.kg^{-1} (B1), or 241 μmol.kg^{-1} (A1F1), the pH variation would reach -0.245 and -0.462 pH unit, respectively, for the Western basin. For the Eastern basin, when C_{ANT} could reach 158 μmol.kg^{-1} (B1), or 266 μmol.kg^{-1} (A1F1), the pH variation would reach -0.242 and -0.457 pH unit, respectively. These variations would remain close to the present amplitude of the observed seasonal variations of pH in the upper layer of the ocean.

One should keep in mind that in this study, the effect of the global warming was not taken into account and consequently, the estimated range of pH variations provides an upper limit. Global warming will somewhat mitigate the exchanges across the ocean-atmosphere interface, thus reducing slightly the penetration of anthropogenic carbon and consequently the Mediterranean Sea acidification. Yet, since the effect of temperature on these equations is relatively small, this study highlights the importance of the thermodynamic equilibriums, which control most of the seawater pH variations.

Although both basins are supersaturated with calcite and aragonite, the calcium carbonate saturation states are lower in the Western basin than those in the Eastern basin. The projected estimates of the calcite and aragonite tipping points ($TP_{\Omega Ar}$, $TP_{\Omega Ca}$) indicate that both basins may become undersaturated with respect to aragonite (and later to calcite), in Mediterranean waters only well after the end of this century.

The last tipping points (TP_{pH7}), would occur when the Mediterranean Sea would become acid (pH<7) due to a large penetration of C_{ANT}.

In summary, this study highlights four tipping points. In each of the Western and Eastern basins of the Mediterranean Sea, these tipping points, calculated at the base of the mixed layer depth, are specific to the location. Nevertheless, they are reached for only slightly different concentrations of C_{ANT}. These points with their limits of C_{ANT} and their significance are as follow:

1) TP_{SD}: when C_{ANT} would reach 86 μmol.kg^{-1} (or as soon as 82 μmol.kg^{-1} for the Western waters), the Mediterranean Sea acidification will intensify sharply,

2) $TP_{\Omega Ar}$: when C_{ANT} would reach 380 μmol.kg^{-1} (or as soon as 317 μmol.kg^{-1} for the Western waters), the

Mediterranean Sea will become undersaturated with respect to aragonite,

3) $TP_{\Omega Ca}$: when C_{ANT} would reach 456 µmol.kg^{-1} (or as soon as 389 µmol.kg^{-1} for the Western waters), the Mediterranean Sea will become undersaturated with respect to calcite,

4) TP_{pH7}: when C_{ANT} would reach 591 µmol.kg^{-1} (or as soon as 548 µmol.kg^{-1} for the Western waters), the Mediterranean Sea will become acid (pH < 7).

When will these tipping points be reached? The first one TP_{SD} has already been reached. The three others $TP_{\Omega Ar}$, $TP_{\Omega Ca}$, and TP_{pH7} will probably be reached within the next (or following) century. The exact timing will strongly depend upon the politics of human activities, which will impact both global warming and the anthropogenic CO_2 raise both in the atmosphere and into the ocean.

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